<div align="center">明　細　書</div>

高結晶性銀粉及びその製造方法

技術分野

[0001]　　本発明は、高結晶性銀粉及びその製造方法に関し、詳しくは、例えば、チップ部品、プラズマディスプレイパネル等の電極や回路を、大幅にファイン化し、高密度及び高精度で且つ高信頼性をもって形成することができる導電性ペースト、特に微細な配線又は薄層で平滑な塗膜等を高密度及び高精度で且つ高信頼性をもって形成することができる導電性ペーストの製造に好ましい、微粒で、分散性がよく、粒度分布がシャープすぎず比較的ブロードであり、結晶子が大きいため、導電性ペーストの原料として用いた場合に、ペーストへの銀粉の分散性及び導電性ペーストにおける銀粉の充填性に優れ、銀厚膜から形成される電極や回路等をよりファイン化することができ、導電性ペーストから得られる銀厚膜が耐熱収縮性に優れると共に比抵抗（抵抗率）の低いものとすることができる高結晶性銀粉及びその製造方法に関するものである。

背景技術

[0002]　　従来、電子部品等の電極や回路を形成する方法として、導電性材料である銀粉をペーストに分散させた導電性ペーストを基板に印刷した後、該ペーストを焼成又はキュアリングし硬化させて銀厚膜を形成することにより回路を形成する方法が知られている。しかし、近年、電子機器の高機能化により電子デバイスの小型高密度化が求められており、このため、導電性ペーストの材料である銀粉にも、導電性ペーストとしたときに微粒でありながら充填性や分散性に優れていることが望まれるようになってきている。なお、本発明において分散性とは、ペーストへの銀粉の分散性のように特に断らない限り、銀粉の一次粒子同士の凝集し難さを意味する。例えば、分散性がよい状態とは一次粒子同士の凝集している割合が少ない又は全くない状態をいい、分散性が悪い状態とは一次粒子同士が凝集している割合が多い又は全て凝集している状態をいう。

[0003]　　上記導電性ペーストが印刷される基板としては、通常はセラミック基板においてICのパッケージ等の発熱が大きい部分等に用いられている。しかし、このセラミック基板

に導電性ペーストを印刷する場合には、セラミック基板の熱収縮率と印刷した導電性ペーストから生成される銀厚膜の熱収縮率とが一般的に異なるため、焼成時においてセラミック基板と銀厚膜とが剥離したり基板自体が変形したりするおそれがある。このため、セラミック基板の熱収縮率と印刷した導電性ペーストから形成される銀厚膜の熱収縮率とは、なるべく近い値を採るものであることが好ましい。

[0004]　このような焼成時における上記銀厚膜の熱収縮の一因としては、導電性ペースト中の銀粉が焼成時に焼結を起こすことにあるものと考えられている。すなわち、銀粉は微小な結晶子から構成される多結晶体であり、銀粉を含む導電性ペーストを銀厚膜の形成のために焼成する際に銀粉中の微小な結晶子が焼結して、銀厚膜の生成前後で寸法変化が生じ熱収縮を起こすものと考えられる。このため、熱収縮の少ない銀粉含有導電性ペーストを得るには、結晶子の焼結がなるべく生じないように、銀粉中の結晶子はできるだけ大きいものであることが望ましい。

[0005]　また、近年、回路の高周波特性の向上や焼成前後における基板の寸法精度をより向上させることが求められており、このため銀厚膜が形成される基板として、上記のような通常のセラミック基板に代えてLTCC（Low　Temperature　Co−fired　Ceramic：低温同時焼成セラミック）基板が用いられるようになってきている。さらに、該LTCC基板は、LTCC基板のグリーンシート（生板）と銀粉等の低抵抗導体を含む導電性ペーストとを同時に焼結させて得られるため、上記の通常のセラミック基板を用いこれに導電性ペーストを印刷して銀厚膜の回路を形成する技術に比べて、焼成回数が少なくて済み、セラミック誘電体膜厚のコントロールが容易になり、導電性ペーストから形成した回路の導体抵抗が低くなり、基板の表面平滑性が向上し易いものとなりこれらの点で好ましい。しかし、LTCCは寸法安定性が非常に優れるため、これに用いる導電性ペーストの材料である銀粉にも熱収縮のより少ないことが強く要求され、従って銀粉中の結晶子の大きいことがより強く望まれている。

[0006]　また、このように銀粉中の結晶子が大きいと、一般的に銀粉の不純物の含有量が低下し、これにより銀厚膜から形成される回路の比抵抗が低くなり易いため、上記のような焼成して形成する回路のみならず非焼成で形成する回路にも銀粉を含む導電性ペーストを用いることが可能になるという点でも好ましいものとなる。

[0007]　上記のように、導電性ペーストに用いられる銀粉には、微粒で、分散性がよく、粒度分布がシャープすぎず比較的ブロードであり、結晶子が大きいことが望まれている。

[0008]　これに対し、特許文献1（特開2000-1706号公報）には、硝酸銀水溶液とアクリル酸モノマーをLアスコルビン酸水溶液に溶解した液とを、混合と同時に反応せしめる高結晶体銀粒子の製造方法が開示されており、該方法によれば、結晶子サイズが400Å以上で、粒径の範囲が2～4μmの狭い範囲にある高結晶性銀粉が得られる。

[0009]　特許文献1：特開2000-1706号公報（第1頁）

発明の開示

発明が解決しようとする課題

[0010]　しかしながら、特許文献1記載の銀粉は、微粒で結晶子も大きいが、例えば700℃程度の高温における熱収縮率が十分に小さくなり難い。この銀粉は、結晶子が十分に大きいにもかかわらず高温における熱収縮率が大きいが、この理由としては、該銀粉の粒径の範囲が2～4μmであり粒度分布がシャープすぎるため銀粉同士に空隙が形成されることにより銀粉の充填性が低くなってしまっていることに起因するものと推測される。このため、導電性ペーストにして銀厚膜の形成やLTCC基板を用いた回路の形成に用いると、回路の形成前後における寸法変化が大きくなり、通常のセラミック基板やLTCC基板、特にLTCC基板において反りが生じ易いという問題があった。

[0011]　従って、本発明の目的は、微粒で、分散性がよく、粒度分布がシャープすぎず比較的ブロードであり、結晶子が大きい高結晶性銀粉、及びその製造方法を提供することにある。

課題を解決するための手段

[0012]　かかる実情において、本発明者は鋭意検討を行った結果、硝酸銀、分散剤及び硝酸を含む第1水溶液と、アスコルビン酸を含む第2水溶液とを混合する方法により銀粉を製造すれば、微粒で、粒度分布がシャープすぎず比較的ブロードであり、結晶子が大きく、導電性ペーストから得られる銀厚膜を耐熱収縮性に優れたものとすることができる高結晶性銀粉が得られることを見出し、本発明を完成するに至った。

[0013]　すなわち、高結晶性銀粉の製造方法は、硝酸銀、分散剤及び硝酸を含む第1水溶

液と、アスコルビン酸を含む第2水溶液とを混合することを特徴とするものである。

[0014] また、上記高結晶性銀粉の製造方法において、前記分散剤がポリビニルピロリドンであることを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0015] また、上記高結晶性銀粉の製造方法において、前記分散剤がゼラチンであることを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0016] また、上記高結晶性銀粉の製造方法において、前記第1水溶液は、硝酸銀100重量部に対して、ポリビニルピロリドンが5重量部〜60重量部、硝酸が35重量部〜70重量部配合されたことを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0017] また、上記高結晶性銀粉の製造方法において、前記第1水溶液は、硝酸銀100重量部に対して、ゼラチンが0.5重量部〜10重量部、硝酸が35重量部〜70重量部配合されたことを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0018] また、上記高結晶性銀粉の製造方法において、前記第1水溶液と前記第2水溶液とを、前記第1水溶液に配合された硝酸銀100重量部に対して、第2水溶液中に配合されたアスコルビン酸が30重量部〜90重量部になる比率で混合することを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0019] また、上記高結晶性銀粉の製造方法において、前記第1水溶液と前記第2水溶液とを、前記第2水溶液に配合されたアスコルビン酸100重量部に対して、第1水溶液中に配合された硝酸が40重量部〜150重量部になる比率で混合することを特徴とする高結晶性銀粉の製造方法を提供するものである。

[0020] また、上記高結晶性銀粉の製造方法において製造されることを特徴とする高結晶性銀粉を提供するものである。

[0021] また、上記高結晶性銀粉の製造方法において製造される高結晶性銀粉であって、結晶子径が300Å以上であることを特徴とするものである。

[0022] また、当該高結晶性銀粉は、平均粒径D_{50}が0.5μm〜10μmであることを特徴とするものである。

[0023] また、当該高結晶性銀粉は、700℃における熱収縮率が±3%以内であることを特徴とするものである。

[0024]　また、当該高結晶性銀粉は、D_{90}/D_{10}が2.1〜5.0であることを特徴とするものである。

[0025]　また、当該高結晶性銀粉は、結晶子径が300Å以上、平均粒径D_{50}が0.5μm〜10μm、700℃における長さ方向の熱収縮率が±3%以内であることを特徴とするものである。

[0026]　また、当該高結晶性銀粉は、D_{90}/D_{10}が2.1〜5.0であることを特徴とするものである。

発明の効果

[0027]　本発明に係る高結晶性銀粉は、微粒で、分散性がよく、粒度分布がシャープすぎず比較的ブロードであり、結晶子が大きいため、導電性ペーストの原料として用いた場合に、ペーストへの銀粉の分散性及び導電性ペーストにおける銀粉の充填性に優れ、銀厚膜から形成される電極や回路等をよりファイン化することができ、導電性ペーストから得られる銀厚膜を耐熱収縮性に優れると共に比抵抗の低いものとすることができる。また、本発明に係る高結晶性銀粉の製造方法は、上記本発明に係る高結晶性銀粉を効率的に製造することができる。

発明を実施するための最良の形態

[0028]　（本発明に係る高結晶性銀粉）

　本発明に係る高結晶性銀粉は、実質的に粒状の粉体である。本発明に係る高結晶性銀粉は、平均粒径D_{50}が0.5μm〜10μm、好ましくは1μm〜5μmである。平均粒径D_{50}が該範囲内にあると、導電性ペーストに用いた場合に導電性ペーストにおける銀粉の充填性に優れると共に銀厚膜から形成される回路等をよりファイン化することができるため好ましい。一方、平均粒径D_{50}が0.5μm未満であると、銀粉の回収が困難になるため好ましくなく、10μmを超えると、銀粉同士が凝集していることが多いため、好ましくない。ここで、平均粒径D_{50}とは、レーザー回折散乱法で求められる体積平均粒径、すなわち累積分布50%における粒径をいう。

[0029]　本発明に係る高結晶性銀粉は、結晶子径が300Å以上、好ましくは350Å〜600Åである。結晶子径が該範囲内にあると、該銀粉を含む導電性ペーストをセラミック基板に塗布し、焼成して銀厚膜からなる回路等を形成した場合に、焼成前後の銀厚

膜の熱収縮率がセラミック基板の熱収縮率と近くなり、銀厚膜がセラミック基板から剥離したりセラミック基板が銀厚膜の寸法変化につられて変形したりすることを抑制する効果が大きいため好ましい。

[0030]　一方、結晶子径が300Å未満であると、該銀粉を含む導電性ペーストをセラミック基板に塗布し、焼成して銀厚膜からなる回路等を形成した場合に、焼成前後の銀厚膜の収縮がセラミック基板の収縮よりも大きくなって、銀厚膜がセラミック基板から剥離したりセラミック基板が銀厚膜の寸法変化につられて変形したりし易いため好ましくない。ここで、結晶子径とは、銀粉試料に対しX線回折を行って得られる、各結晶面の回折角のピークの半値幅から求められる結晶子径の平均値をいう。

[0031]　本発明に係る高結晶性銀粉は、D_{90}/D_{10}が通常2.1〜5.0、好ましくは2.5〜4.7である。なお、本発明において、D_{10}及びD_{90}は、それぞれ、レーザー回折散乱式粒度分布測定法による累積分布10容量％及び90容量％におけるメジアン径（μm）を示す。D_{90}/D_{10}はバラツキを示す指標であり、D_{90}/D_{10}が大きいと粒度分布のバラツキが大きいことを示す。D_{90}/D_{10}が上記範囲内にあると、銀粉の粒度分布がシャープすぎず比較的ブロードになり、該銀粉を用いた導電性ペーストで回路を形成すると銀粉の充填性が優れるため回路の耐熱収縮性が優れたもの、すなわち、焼成前後における回路の寸法変化が小さいものとなり易いため好ましい。

[0032]　一方、D_{90}/D_{10}が2.1未満であると、銀粉の粒度分布がシャープになりすぎて、該銀粉を用いた導電性ペーストで回路を形成すると銀粉の充填性が劣るため回路の耐熱収縮性が悪化したもの、すなわち、焼成前後における回路の寸法変化が大きいものとなり易いため好ましくない。また、D_{90}/D_{10}が5.0を超えると、銀粉の粒度分布がブロードになりすぎて、該銀粉を用いた導電性ペーストで回路を形成すると銀粉の充填性が劣るため回路の耐熱収縮性が悪化したもの、すなわち、焼成前後における回路の寸法変化が大きいものとなり易いため好ましくない。

[0033]　本発明に係る高結晶性銀粉は、700℃における長さ方向の熱収縮率が、通常±3％以内、好ましくは±2％以内である。なお、本発明において±X％以内とは、−X％〜＋X％であることを意味する。本発明において、700℃における長さ方向の熱収縮率とは、銀粉をペレットに形成した試料について、熱機械的分析（TMA）を用いて測

定したペレットの長さ方向の熱収縮率をいう。

[0034]　本発明に係る高結晶性銀粉は、比較的低温、例えば300℃で焼成した銀塗膜の抵抗率が低い。すなわち、高結晶性銀粉を低温で焼結させても焼結物の抵抗率が小さくなり易い。なお、このように300℃で焼成した銀塗膜の抵抗率が低い理由は、結晶子径が大きいことにより銀粉内の電子の動きがスムーズになるためであると推測される。

[0035]　本発明に係る高結晶性銀粉は、比表面積が通常$0.10m^2/g$〜$1.0m^2/g$、好ましくは$0.20m^2/g$〜$0.90m^2/g$である。該比表面積が$0.10m^2/g$未満であると、銀厚膜による電極や回路のファイン化が困難になり易いため好ましくない。また、該比表面積が$1.0m^2/g$を超えると、銀粉のペースト化が困難になり易いため好ましくない。本発明において比表面積とは、BET比表面積をいう。

[0036]　本発明に係る高結晶性銀粉は、タップ密度が通常$3.8g/cm^3$以上、好ましくは4.0〜$6.0g/cm^3$である。タップ密度が該範囲内にあると、導電性ペーストの作製の際に高結晶性銀粉のペーストへの銀粉の充填性が良好で導電性ペーストの作製が容易であり、また導電性ペーストの塗膜形成の際に高結晶性銀粉間に適度な空隙が形成されることにより塗膜を焼成する際に塗膜からの脱バイが容易に行われて焼成膜密度が向上し、この結果銀厚膜の抵抗を低くし易いため好ましい。本発明に係る高結晶性銀粉は、例えば、下記の方法により製造することができる。

[0037]　（本発明に係る高結晶性銀粉の製造方法）

　本発明に係る高結晶性銀粉の製造方法は、硝酸銀、分散剤及び硝酸を含む第1水溶液と、アスコルビン酸を含む第2水溶液とを混合するものである。

[0038]　本発明において第1水溶液とは、硝酸銀、分散剤及び硝酸を含む水溶液をいう。第1水溶液の調製に用いられる水としては、純水、イオン交換水、超純水等が、銀粉への不純物の混入防止のため好ましい。本発明で用いられる硝酸銀としては、特に限定されず、固形のもの及び水溶液にしたもののいずれも用いることができる。

[0039]　本発明で用いられる分散剤としては、例えば、ポリビニルピロリドン（PVP）、ゼラチン、ポリエチレングリコール、ポリビニルアルコール等が挙げられる。なお、本発明においてゼラチンとはニカワを含む概念で用いる。本発明で用いられる分散剤のうち、

ポリビニルピロリドン、ゼラチンが銀粉の耐熱収縮性を特に高くすることができるため好ましい。本発明においては、第1水溶液に分散剤を配合することにより、銀粉の分散性を向上させると共に、銀粉が微粒でその粒度分布をシャープすぎず比較的ブロードにする作用がある。

[0040]　　本発明で用いられる硝酸としては、特に限定されず、濃硝酸、希硝酸のいずれも用いることができる。本発明においては、第1水溶液に硝酸を配合することにより、銀イオンから銀を生成する反応速度が比較的遅くなるように制御されるため、銀粉の粒度分布をシャープすぎず比較的ブロードにし、且つ結晶子を大きくする作用がある。なお、硝酸を配合せずに銀粉を製造すると、銀イオンから銀を生成する反応速度が速すぎて反応が直ちに生じるため、本発明のように硝酸を配合して製造する場合に比べて、得られる銀粉は、粒径が小さく、且つ、結晶子径が小さくなり易い。

[0041]　　第1水溶液は、分散剤がポリビニルピロリドンである場合、硝酸銀100重量部に対して、ポリビニルピロリドンを通常5重量部〜60重量部、好ましくは15重量部〜50重量部、さらに好ましくは20重量部〜40重量部含む。ポリビニルピロリドンの配合量が該範囲内にあると、銀粉の分散性を向上させると共に、銀粉の粒度分布がシャープすぎず比較的ブロードになり易いため好ましい。一方、ポリビニルピロリドンの配合量が5重量部未満であると得られる銀粉が凝集し易いため好ましくなく、60重量部を超えると得られる銀粉中の不純物濃度が高くなり易く、環境を汚染し易く、生産コストが高くなり易いため好ましくない。

[0042]　　第1水溶液は、分散剤がゼラチンである場合、硝酸銀100重量部に対して、ゼラチンを通常0.5重量部〜10重量部、好ましくは1重量部〜8重量部、さらに好ましくは2重量部〜6重量部含む。ゼラチンの配合量が該範囲内にあると、銀粉の分散性を向上させると共に、銀粉の粒度分布がシャープすぎず比較的ブロードになり易いため好ましい。一方、ゼラチンの配合量が0.5重量部未満であると得られる銀粉が凝集し易いため好ましくなく、10重量部を超えると得られる銀粉中の不純物濃度が高くなり易く、環境を汚染し易く、生産コストが高くなり易いため好ましくない。

[0043]　　第1水溶液は、分散剤がポリビニルピロリドンである場合、水100重量部に対しゼラチンを、通常1重量部〜10重量部、好ましくは2重量部〜4重量部含む。ポリビニル

ピロリドンの配合量が該範囲内にあると、銀粉の分散性を向上させると共に、銀粉の
粒度分布がシャープすぎず比較的ブロードになり易いため好ましい。一方、ポリビニ
ルピロリドンの配合量が1重量部未満であると得られる銀粉が凝集し易いため好ましく
なく、10重量部を超えると得られる銀粉中の不純物濃度が高くなり易く、環境を汚染
し易く、生産コストが高くなり易いため好ましくない。

[0044]　　第1水溶液は、分散剤がゼラチンである場合、水100重量部に対しゼラチンを、通
常0.1重量部〜5重量部、好ましくは0.4重量部〜2重量部含む。ゼラチンの配合
量が該範囲内にあると、銀粉の分散性を向上させると共に、銀粉の粒度分布がシャ
ープすぎず比較的ブロードになり易いため好ましい。一方、ゼラチンの配合量が0.1
重量部未満であると得られる銀粉が凝集し易いため好ましくなく、5重量部を超えると
得られる銀粉中の不純物濃度が高くなり易く、環境を汚染し易く、生産コストが高くな
り易いため好ましくない。

[0045]　　第1水溶液は、硝酸銀100重量部に対して、硝酸を、通常35重量部〜70重量部、
好ましくは40重量部〜60重量部、さらに好ましくは48重量部〜54重量部含む。硝
酸の配合量が該範囲内にあると、銀粉の粒度分布がシャープすぎず比較的ブロード
になり、且つ結晶子を大きくする効果が大きいため好ましい。一方、硝酸の配合量が
35重量部未満であると銀粉の結晶性が低くなり易いため好ましくなく、70重量部を
超えると得られる銀粉が凝集し易いため好ましくない。なお、本発明において硝酸の
配合量とは、濃度61%の濃硝酸に換算した配合量を意味する。

[0046]　　本発明において第2水溶液とは、アスコルビン酸を含む水溶液をいう。第2水溶液
の調製に用いられる水としては、純水、イオン交換水、超純水等が、銀粉への不純物
の混入防止のため好ましい。本発明で用いられるアスコルビン酸としては、L体、D体
のいずれも用いることができる。

[0047]　　本発明に係る製造方法では、上記第1水溶液と第2水溶液とを混合して、混合液中
で高結晶性銀粉を析出させる。混合形態としては、例えば、第1水溶液を撹拌してお
きこれに第2水溶液を添加する方法が挙げられる。この場合の第2水溶液の添加方
法としては、第2水溶液の全量を第1水溶液に一括添加してもよいし、第2水溶液を
少量ずつ第1水溶液に徐々に添加してもよい。なお、第1水溶液中の分散剤がポリビ

ニルピロリドンである場合は、第2水溶液の全量を第1水溶液に一括添加する方法を採用すると微粒で粒度分布がシャープすぎず比較的ブロードである銀粉を得易いため好ましく、第1水溶液中の分散剤がゼラチンである場合は、第2水溶液を少量ずつ第1水溶液に徐々に添加する方法を採用すると銀粉の粒径の制御をし易いため好ましい。

[0048]　　第1水溶液と第2水溶液との混合においては、第1水溶液に配合された硝酸銀100重量部に対して、第2水溶液中に配合されたアスコルビン酸が、通常30重量部〜90重量部、好ましくは40重量部〜80重量部、さらに好ましくは50重量部〜75重量部になる比率で混合する。硝酸銀に対するアスコルビン酸の配合量が該範囲内にあると、銀粉の収率が高くなり易いため好ましい。一方、硝酸銀100重量部に対するアスコルビン酸の配合量が30重量部未満であると還元が不十分で銀粉の収率が低くなり易いため好ましくなく、硝酸銀100重量部に対するアスコルビン酸の配合量が90重量を超えると環境を汚染し易く、生産コストが高くなり易いため好ましくない。

[0049]　　また、第1水溶液と第2水溶液との混合においては、得られた混合液中の銀イオン濃度が、通常10g／l〜80g／l、好ましくは30g／l〜65g／lになる比率で混合する。混合液中の銀イオン濃度が該範囲内にあると、銀粉の収率が高く且つ得られる銀粉が凝集し難いため好ましい。一方、銀イオン濃度が10g／l未満であると銀粉の生産性が悪くなり易いため好ましくなく、銀イオン濃度が80g／lを超えると得られる銀粉が凝集し易いため好ましくない。

[0050]　　また、第1水溶液と第2水溶液との混合においては、第2水溶液に配合されたアスコルビン酸100重量部に対して、第1水溶液中に配合された硝酸が、通常40重量部〜150重量部、好ましくは50重量部〜120重量部、さらに好ましくは65重量部〜100重量部になる比率で混合する。アスコルビン酸に対する硝酸の配合量が該範囲内にあると、銀粉の収率が高くなり易いため好ましい。一方、アスコルビン酸100重量部に対する硝酸の配合量が40重量部未満であると得られる銀粉の結晶子径を十分に大きくさせることが困難であるため好ましくなく、アスコルビン酸100重量部に対する硝酸の配合量が150重量部を超えると得られる銀粉が凝集し易いため好ましくない。

[0051]　　第1水溶液と第2水溶液との混合により、混合液中に析出した銀粉は、第1水溶液と

第2水溶液との混合終了後、混合液をさらに通常3分間以上、好ましくは5分間〜10分間混合続けることにより混合液中で銀粉を成長させると、銀粉の粒径及び粒度分布並びに分散性が、本発明に係る銀粉の特定範囲内のものとなり易いため好ましい。混合液中に得られた銀粉は、例えば、ヌッチェ等の濾過手段で濾過した後、濾滓を純水で洗浄し、乾燥すると、本発明に係る高結晶性銀粉が得られる。

[0052]　　上記本発明に係る高結晶性銀粉は、例えば、チップ部品、プラズマディスプレイパネル、ガラスセラミックパッケージ、セラミックフィルター等の電極や回路を形成することができる導電性ペーストの原料として使用することができ、特に、銀粉の熱収縮率が非常に小さいことを利用して、回路を形成する基板として通常のセラミック基板のみならず、LTCC基板用の導電性ペーストの原料として好適に使用することができる。また、本発明に係る高結晶性銀粉の製造方法は、本発明に係る高結晶性銀粉の製造に使用することができる。

[0053]　　以下に実施例を示すが、本発明はこれらに限定されて解釈されるものではない。

実施例 1

[0054]　　常温の純水500gにPVP（K価：30）10g、硝酸銀50g及び濃硝酸（濃度61%）24.6gを入れ、攪拌し溶解して第1水溶液を調製した（第1水溶液A）。一方、常温の純水500gにアスコルビン酸35.8gを入れ、攪拌し溶解して第2水溶液を調製した（第2水溶液A）。第1水溶液及び第2水溶液の組成を表1及び表2に示す。

　　次に、第1水溶液Aを攪拌した状態にし、該第1水溶液Aに第2水溶液Aを一括添加し、添加終了後からさらに5分間攪拌して混合液中で粒子を成長させた。その後攪拌を止め、混合液中の粒子を沈降させた後、混合液の上澄みを捨て、混合液をヌッチェを用いて濾過し、濾滓を純水で洗浄し、乾燥して、高結晶性銀粉を得た。

　　得られた銀粉について、D_{10}、D_{50}、D_{90}、D_{100}、SD、結晶子径、比表面積、タップ密度、熱収縮率及び抵抗率を下記方法により測定し、D_{90}/D_{10}を算出した。結果を表3〜表6に示す。

[0055]　　（D_{10}、D_{50}、D_{90}、D_{100}、SD）：日機装株式会社製マイクロトラックHRAを用いて、レーザー回折散乱法で求められる累積分布が10%、50%、90%及び100%の時点における粒径を、それぞれD_{10}（μm）、D_{50}（μm）、D_{90}（μm）、D_{100}（μm）とし、得ら

れた粒度分布の標準偏差をSDとした。

（結晶子径）：リガク株式会社製X線回折装置RINT2000PCを用いて粉末X線回折を行い、得られた各結晶面の回折角のピークの半値幅から結晶子径を求めた。

（比表面積）：ユアサアイオニクス株式会社製モノソーブを用いて測定したBET比表面積を用いた。

（タップ密度）：蔵持科学機械製作所製タップデンサーを用いて試料をタッピングすることによりタップ密度を測定した。

（熱収縮率）：銀粉を押し固めて円柱状のペレットを作製し、セイコーインスツルメンツ株式会社製TMA／SS6300を用い、該ペレットについて、Air（空気）中、昇温速度10℃／minで常温から850℃までの範囲でTMA分析を行い、ペレットの長さ方向の熱収縮率を測定した。測定温度は300℃、500℃及び700℃とした。

（抵抗率）：ターピネオール95重量部とエチルセルロース5重量部とを混合して混合溶媒を調製し、該混合溶媒15重量部と試料粉体85重量部とを混合してペーストを作製し、該ペーストを300℃で焼成して数μm程度の厚みを有する銀塗膜を作製した。また、焼成温度を300℃に代えて、400℃及び500℃とした以外は上記と同様にして銀塗膜を作製した。

次いで、（Hewlett−Packard株式会社製、MILLIOHM METER）を用いて、四端子法で上記銀塗膜の抵抗（Ω）を測定した後、銀塗膜の断面積と端子間の長さとから抵抗率ρ（Ω・m）を求めた。

実施例2

[0056]　常温の純水500gにPVP（K価：30）20g、硝酸銀50g及び濃硝酸（濃度61%）24.6gを入れ、攪拌し溶解して第1水溶液を調製した（第1水溶液B）。一方、常温の純水500gにアスコルビン酸35.8gを入れ、攪拌し溶解して第2水溶液を調製した（第2水溶液A）。第1水溶液及び第2水溶液の組成を表1及び表2に示す。

次に、第1水溶液Bを攪拌した状態にし、該第1水溶液Bに第2水溶液Aを一括添加し、添加終了後からさらに5分間攪拌して混合液中で粒子を成長させた。その後攪拌を止め、混合液中の粒子を沈降させた後、混合液の上澄みを捨て、混合液をヌッチェを用いて濾過し、濾滓を純水で洗浄し、乾燥して、高結晶性銀粉を得た。

得られた銀粉について、実施例1と同様にして、D_{10}、D_{50}、D_{90}、D_{100}、SD、結晶子径、比表面積、タップ密度、熱収縮率及び抵抗率を下記方法により測定し、D_{90}/D_{10}を算出した。結果を表3〜表6に示す。

比較例1

[0057]　常温の純水500gにPVP（K価：30）10g及び硝酸銀50gを入れ、攪拌し溶解して第1水溶液を調製した（第1水溶液C）。一方、常温の純水500gにアスコルビン酸26gを入れ、攪拌し溶解して第2水溶液を調製した（第2水溶液B）。第1水溶液及び第2水溶液の組成を表1及び表2に示す。

次に、第1水溶液Cを攪拌した状態にし、該第1水溶液Cに第2水溶液Bを一括添加し、添加終了後からさらに5分間攪拌して混合液中で粒子を成長させた。その後攪拌を止め、混合液中の粒子を沈降させた後、混合液の上澄みを捨て、混合液をヌッチェを用いて濾過し、濾滓を純水で洗浄し、乾燥して、銀粉を得た。

得られた銀粉について、実施例1と同様にして、D_{10}、D_{50}、D_{90}、D_{100}、SD、結晶子径、比表面積、タップ密度、熱収縮率及び抵抗率を下記方法により測定し、D_{90}/D_{10}を算出した。結果を表3〜表6に示す。

実施例3

[0058]　常温の純水250gにゼラチン（新田ゼラチン株式会社製）1.0g、硝酸銀50g及び濃硝酸（濃度61%）26.4gを入れ、50℃まで加熱し攪拌することによりこれらを溶解して第1水溶液を調製した（第1水溶液D）。一方、常温の純水250gにアスコルビン酸26.4gを入れ、攪拌し溶解して第2水溶液を調製した（第2水溶液C）。第1水溶液及び第2水溶液の組成を表1及び表2に示す。

次に、50℃の第1水溶液Dを攪拌した状態にし、該第1水溶液Dに常温の第2水溶液Cを30分かけて徐々に添加し、添加終了後からさらに5分間攪拌して混合液中で粒子を成長させた。その後攪拌を止め、混合液中の粒子を沈降させた後、混合液の上澄みを捨て、混合液をヌッチェを用いて濾過し、濾滓を純水で洗浄し、乾燥して、高結晶性銀粉を得た。

得られた銀粉について、実施例1と同様にして、D_{10}、D_{50}、D_{90}、D_{100}、SD、結晶子径、比表面積、タップ密度、熱収縮率及び抵抗率を下記方法により測定し、D_{90}/D_{10}

を算出した。結果を表3〜表6に示す。

実施例4

[0059]　　常温の純水500gにゼラチン（新田ゼラチン株式会社製）3．0g、硝酸銀50g及び濃硝酸（濃度61％）24．6gを入れ、50℃まで加熱し攪拌することによりこれらを溶解して第1水溶液を調製した（第1水溶液E）。一方、常温の純水500gにアスコルビン酸25．9gを入れ、攪拌し溶解して第2水溶液を調製した（第2水溶液D）。第1水溶液及び第2水溶液の組成を表1及び表2に示す。

　　次に、50℃の第1水溶液Eを攪拌した状態にし、該第1水溶液Eに常温の第2水溶液Dを30分かけて徐々に添加し、添加終了後からさらに5分間攪拌して混合液中で粒子を成長させた。その後攪拌を止め、混合液中の粒子を沈降させた後、混合液の上澄みを捨て、混合液をヌッチェを用いて濾過し、濾滓を純水で洗浄し、乾燥して、高結晶性銀粉を得た。

　　得られた銀粉について、実施例1と同様にして、D_{10}、D_{50}、D_{90}、D_{100}、SD、結晶子径、比表面積、タップ密度、熱収縮率及び抵抗率を下記方法により測定し、D_{90}/D_{10}を算出した。結果を表3〜表6に示す。

[0060]　[表1]

	水（g）	分散剤の種類	分散剤（g）	硝酸銀（g）	濃硝酸（g）	第1水溶液の種類
実施例1	500	PVP	10	50	24．6	A
実施例2	500	PVP	20	50	24．6	B
比較例1	500	PVP	10	50	0	C
実施例3	250	ゼラチン	1．0	50	26．4	D
実施例4	500	ゼラチン	3．0	50	24．6	E

[0061]　[表2]

	水 （g）	アスコルビン酸 （g）	第2水溶液の種類
実施例1	500	35.8	A
実施例2	500	35.8	A
比較例1	500	26.0	B
実施例3	250	26.4	C
実施例4	500	25.9	D

[0062] ［表3］

	D_{10} （μm）	D_{50} （μm）	D_{90} （μm）	D_{100} （μm）	D_{90}/D_{10}	SD
実施例1	2.97	6.35	10.75	22.0	3.6	3.01
実施例2	1.30	3.03	5.67	15.6	4.4	1.59
比較例1	2.14	2.83	4.08	9.3	1.9	0.71
実施例3	2.72	4.36	7.33	18.5	2.7	1.71
実施例4	0.76	1.27	2.28	4.6	3.0	0.57

[0063] ［表4］

	結晶子径 （Å）	比表面積 （m²/g）	タップ密度 （g/cm³）
実施例1	441	0.30	4.1
実施例2	377	0.62	4.0
比較例1	258	0.62	3.8
実施例3	545	0.20	4.4
実施例4	441	0.72	4.8

[0064] ［表5］

	３００℃における熱収縮率（％）	５００℃における熱収縮率（％）	７００℃における熱収縮率（％）
実施例1	0.13	-2.13	-2.2
実施例2	0.09	-2.68	-2.9
比較例1	0.84	-4.02	-7.82
実施例3	0.27	1.08	1.13
実施例4	-0.58	-1.51	-1.35

[0065]　[表6]

	３００℃で焼成した銀塗膜の抵抗率 ρ（Ω・m）	４００℃で焼成した銀塗膜の抵抗率 ρ（Ω・m）	５００℃で焼成した銀塗膜の抵抗率 ρ（Ω・m）
実施例1	4.1×10^{-5}	2.0×10^{-5}	9.9×10^{-6}
実施例2	5.2×10^{-5}	1.5×10^{-5}	1.2×10^{-5}
比較例1	7.2×10^{-4}	8.9×10^{-6}	4.8×10^{-5}
実施例3	9.4×10^{-6}	8.3×10^{-6}	9.9×10^{-6}
実施例4	1.0×10^{-5}	8.8×10^{-6}	4.8×10^{-5}

[0066]　　表1～表5より、分散剤及び硝酸を用いて作製した銀粉は、結晶子径が大きくて高結晶性であり、700℃における熱収縮率が小さいことが判る。また、分散剤としてゼラチンを用いたものは、特に700℃における熱収縮率が小さいことが判る。また、表6より、分散剤及び硝酸を用いて作製した銀粉は、硝酸を用いずに作製した銀粉に比べて、300℃で焼成した銀塗膜の抵抗率 ρ が低いことが判る。この理由は、結晶子径が大きいことにより銀粉内の電子の動きがスムーズになるためであると推測される。

産業上の利用可能性

[0067]　　本発明に係る高結晶性銀粉及び高結晶性銀粉の製造方法は、例えば、チップ部

品、プラズマディスプレイパネル、ガラスセラミックパッケージ、セラミックフィルター等の電極や回路を形成することができる導電性ペーストの原料として使用することができ、特に、LTCC基板用の導電性ペーストの原料として好適に使用することができる。

請求の範囲

[1]　　硝酸銀、分散剤及び硝酸を含む第1水溶液と、アスコルビン酸を含む第2水溶液とを混合することを特徴とする高結晶性銀粉の製造方法。

[2]　　前記分散剤がポリビニルピロリドンであることを特徴とする請求項1記載の高結晶性銀粉の製造方法。

[3]　　前記分散剤がゼラチンであることを特徴とする請求項1記載の高結晶性銀粉の製造方法。

[4]　　前記第1水溶液は、硝酸銀100重量部に対して、ポリビニルピロリドンが5重量部〜60重量部、硝酸が35重量部〜70重量部配合されたことを特徴とする請求項2記載の高結晶性銀粉の製造方法。

[5]　　前記第1水溶液は、硝酸銀100重量部に対して、ゼラチンが0.5重量部〜10重量部、硝酸が35重量部〜70重量部配合されたことを特徴とする請求項3記載の高結晶性銀粉の製造方法。

[6]　　前記第1水溶液と前記第2水溶液とを、前記第1水溶液に配合された硝酸銀100重量部に対して、第2水溶液中に配合されたアスコルビン酸が30重量部〜90重量部になる比率で混合することを特徴とする請求項1記載の高結晶性銀粉の製造方法。

[7]　　前記第1水溶液と前記第2水溶液とを、前記第2水溶液に配合されたアスコルビン酸100重量部に対して、第1水溶液中に配合された硝酸が40重量部〜150重量部になる比率で混合することを特徴とする請求項1記載の高結晶性銀粉の製造方法。

[8]　　請求項1に記載の方法で製造されることを特徴とする高結晶性銀粉。

[9]　　結晶子径が300Å以上であることを特徴とする請求項8記載の高結晶性銀粉。

[10]　　平均粒径D_{50}が0.5μm〜10μmであることを特徴とする請求項8記載の高結晶性銀粉。

　　　（ただし、D_{50}は、レーザー回折散乱式粒度分布測定法による累積分布50容量%におけるメジアン径（μm）を示す。）

[11]　　700℃における熱収縮率が±3%以内であることを特徴とする請求項8記載の高結晶性銀粉。

[12]　　$D_{90}／D_{10}$が2.1〜5.0であることを特徴とする請求項8記載の高結晶性銀粉。

（ただし、前記式において、D_{10}及びD_{90}は、それぞれ、レーザー回折散乱式粒度分布測定法による累積分布10容量％及び90容量％におけるメジアン径（μm）を示す。）

[13]　結晶子径が300Å以上、平均粒径D_{50}が0.5μm〜10μm、700℃における長さ方向の熱収縮率が±3％以内であることを特徴とする高結晶性銀粉。

[14]　D_{90}／D_{10}が2.1〜5.0であることを特徴とする請求項13記載の高結晶性銀粉。
　　　（ただし、前記式において、D_{10}及びD_{90}は、それぞれ、レーザー回折散乱式粒度分布測定法による累積分布10容量％及び90容量％におけるメジアン径（μm）を示す。）

国際出願番号　PCT／JP2005／001660

A.	発明の属する分野の分類（国際特許分類（IPC））

Int.Cl.7　B22F9/24, 1/00

B.	調査を行った分野

調査を行った最小限資料（国際特許分類（IPC））

Int.Cl.7　B22F9/24, 1/00

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報　　　　　　　１９２２－１９９６年
日本国公開実用新案公報　　　　　１９７１－２００５年
日本国実用新案登録公報　　　　　１９９６－２００５年
日本国登録実用新案公報　　　　　１９９４－２００５年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

C.	関連すると認められる文献	
引用文献の カテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
X Y	JP 01-104338 A（田中貴金属工業株式会社）1989.04.21, 特許請求の範囲　（ファミリーなし）	1, 8-14 1-14
Y	JP 63-307206 A（田中貴金属工業株式会社）1988.12.14, 特許請求の範囲、実施例　（ファミリーなし）	1-14
Y	JP 2000-001706 A（田中貴金属工業株式会社） 2000.01.07, 特許請求の範囲、第００１１段落　（ファミリーなし）	1-14

☐　C欄の続きにも文献が列挙されている。　　　　　　☐　パテントファミリーに関する別紙を参照。

＊　引用文献のカテゴリー
「A」特に関連のある文献ではなく、一般的技術水準を示す
　　もの
「E」国際出願日前の出願または特許であるが、国際出願日
　　以後に公表されたもの
「L」優先権主張に疑義を提起する文献又は他の文献の発行
　　日若しくは他の特別な理由を確立するために引用す
　　る文献（理由を付す）
「O」口頭による開示、使用、展示等に言及する文献
「P」国際出願日前で、かつ優先権の主張の基礎となる出願

の日の後に公表された文献
「T」国際出願日又は優先日後に公表された文献であって
　　出願と矛盾するものではなく、発明の原理又は理論
　　の理解のために引用するもの
「X」特に関連のある文献であって、当該文献のみで発明
　　の新規性又は進歩性がないと考えられるもの
「Y」特に関連のある文献であって、当該文献と他の１以
　　上の文献との、当業者にとって自明である組合せに
　　よって進歩性がないと考えられるもの
「＆」同一パテントファミリー文献

国際調査を完了した日 　　　　２５．０４．２００５．	国際調査報告の発送日 　　１７．５．２００５		
国際調査機関の名称及びあて先 　　日本国特許庁（ISA／JP） 　　　郵便番号１００－８９１５ 　　　東京都千代田区霞が関三丁目４番３号	特許庁審査官（権限のある職員） 　　米田　健志	4K	8924
	電話番号　０３－３５８１－１１０１　内線　３４３５		

様式PCT／ISA／210（第2ページ）（2004年1月）

DESCRIPTION

HIGHLY CRYSTALLINE SILVER POWDER AND METHOD FOR PRODUCING THE SAME

Technical Field

[0001]

The present invention relates to highly crystalline silver powder and a method for producing the same, and more specifically, to highly crystalline silver powder preferable for production of a conductive paste that can significantly reduce the size of the electrode or circuit of, for example, a chip devices, plasma display panel and the like with high density, high accuracy and high reliability. In particular it can enable to form a minute wiring or a thin and flat coating film with high density, high accuracy and high reliability. It is because the silver powder is composed of fine particles, has high dispersibility, particle size distribution is not excessively sharp but is relatively broad, and crystallites are large. So when it is used as the material for the conductive paste, the dispersibility of the silver powder and the filling properties of the paste are excellent, and then the size of the electrode or circuit formed from the thick silver film can be reduced, and the thick silver film obtained from the conductive

paste excels in thermal shrinkage resistance, and has low specific resistance (resistivity).

Background Art

[0002]

Heretofore, as a method for forming an electrode or circuit of an electronic part or the like, there has been known a method to form a circuit by printing a conductive paste wherein silver powder, which is a conductive material, is dispersed in a paste, on a substrate, and baking or curing the paste to form a thick silver film. However in recent years, due to the improvement in functions of electronic equipment, so called down sizing and wiring density increase of electronic devices have been demanded; consequently, it has been desired that silver powder, which is the material for the conductive paste, excels in filling properties and dispersibility despite of fine particles when used in the conductive paste. In the present invention, dispersibility means the difficulty of aggregating the primary particles of the silver powder with each other, unless otherwise specified such as the dispersibility of silver powder in a paste. For example, the state of high dispersibility means the state wherein there is little or no proportion of primary particles are aggregated with each other; and the state of low dispersibility means the state wherein

there is much proportion or all of aggregated primary particles are aggregated with each other.

[0003]

A substrate on which the above-described conductive paste is printed is normally used in a part of a ceramic substrate where heat generation is large, such as the IC package. However, when the conductive paste is printed on the ceramic substrate, since the thermal shrinkage of the ceramic substrate is generally different from the thermal shrinkage of the thick silver film formed from the conductive paste, there is possibility wherein the thick silver film is separated from the ceramic substrate, or the substrate itself is deformed. Therefore, it is preferable that the rate of the thermal shrinkage of the ceramic substrate is as close to the rate of the thermal shrinkage of the thick silver film formed from the conductive paste.

[0004]

As a cause of the thermal shrinkage of the above-described thick silver film in such baking process, it is considered that the silver powder in the conductive paste causes sintering during baking. Specifically, it is considered that the silver powder is a polycrystalline construction composed of fine crystallites, and when the conductive paste containing silver powder is baked for the formation of the thick silver film, the fine crystallites in the silver powder are sintered, and

dimension change between before and after formation of the sintered thick silver film cause thermal shrinkage. Therefore, in order to obtain a conductive paste containing silver powder with less thermal shrinkage, it is desirable that the crystallites in the silver powder are as large as possible so as to minimize the sintering of the crystallites.

[0005]

In recent years, the improvement of the high-frequency signal characteristics of circuits and the improvement of dimensional stability of substrates before and after sintering are demanded, and for this, as a substrate on which the thick silver film is formed, an LTCC (low temperature co-baked ceramic) substrate has been used substituting the above-described ordinary ceramic substrates. Furthermore, since the LTCC substrate is obtained by sintering a green sheet of the LTCC substrate with a conductive paste containing a low-resistance conductor such as silver powder together, compared with the technique to form the circuit of a thick silver film by printing a conductive paste using the above-described ordinary ceramic substrate, the number of sintering steps is less, the film thickness of the ceramic dielectric can be easily controlled, the conductor resistance of the circuit formed from the conductive paste is lowered, and the coplanarity of the substrate can be easily improved. However, since the

LTCC is much excellent in dimensional stability, silver powder, which is the material of the conductive paste used in it is strongly required to have less thermal shrinkage, and therefore, it is strongly desired that the crystallites in the silver powder be large.

[0006]

If the crystallites in the silver powder are large as described above, the content of impurities in the silver powder is generally lowered, and thereby the specific resistance of the circuit formed from the thick silver film is easily lowered; therefore, this is also preferable in the aspect that the conductive paste containing silver powder can be used not only in the circuit formed by baking as described above, but also in the circuit formed without baking.

[0007]

As described above, it is desired for silver powder used in the conductive paste, that the silver powder which is composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large.

[0008]

Whereas in Patent Document 1 (Japanese Patent Laid-Open No. 2000-1706), a method for producing highly crystalline silver powder wherein an aqueous solution of silver nitrate and a solution prepared by dissolving

acrylic acid monomer in an aqueous solution of L-ascorbic acid are mixed and allowed to react simultaneously. According to the above-described method, highly crystalline silver powder whose crystallite size is 400 Å or more, and the range of the particle diameters is as narrow as 2 to 4 μm can be obtained.

[0009]

    Patent Document 1: Japanese Patent Laid-Open No. 2000-1706 (page 1)

Disclosure of the Invention

Problems to be Solved by the Invention

[0010]

    However, although the silver powder described in Patent Document 1 is composed of fine particles with large crystallites, it is difficult that the thermal shrinkage at a high temperature of for example about 700°C is sufficiently reduced. The silver powder has a large thermal shrinkage at a high temperature even if the crystallites are sufficiently large, and the reason is estimated to be caused by that the range of the particle diameters of the silver powder is between 2 and 4 μm, and since the particle size distribution is excessively sharp, gaps are formed between the particles of the silver powder, and the filling of the silver powder is lowered. Therefore, when the silver powder was used to prepare a conductive paste to form a thick silver film or to form a

circuit using an LTCC substrate, the dimension change between before and after forming the circuit was enlarged causing a problem of warpage in an ordinary ceramic substrate or LTCC substrate, particularly the LTCC substrate.

[0011]

Therefore, it is an object of the present invention to provide highly crystalline silver powder composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large; and a method for producing the same.

Means for Solving the Problems

[0012]

Under such a situation, the present inventors carried out keen studies, and found to complete the present invention. It is that if silver powder is produced using a method to mix a first aqueous solution containing silver nitrate, a dispersing agent and nitric acid, and a second aqueous solution containing ascorbic acid, highly crystalline silver powder composed of fine particles, having high dispersibility, whose particle size distribution is not excessively sharp but relatively broad, and the crystallites are large. And it can make the thick silver film obtained from the conductive paste excel in thermal shrinkage resistance, can be obtained.

[0013]

Specifically, the present invention provides a
method for producing highly crystalline silver powder
which is characterized in that mixing a first aqueous
solution and a second aqueous solution, wherein the first
aqueous solution contains silver nitrate, a dispersing
agent and nitric acid, and the second solution contains
ascorbic acid.

[0014]

The present invention also provides the method for
producing highly crystalline silver powder characterized
in that the dispersing agent is polyvinylpyrrolidone.

[0015]

The present invention function provides the method
for producing highly crystalline silver powder
characterized in that the dispersing agent is a gelatin.

[0016]

The present invention still further provides the
method for producing highly crystalline silver powder
characterized in that the first aqueous solution when it
contains 100 parts by weight of silver nitrate, it
further contains 5 parts by weight to 60 parts by weight
of polyvinylpyrrolidone and 35 parts by weight to 70
parts by weight of nitric acid.

[0017]

The present invention also provides the method for
producing highly crystalline silver powder characterized
in that the first aqueous solution when it contains 100

parts by weight of silver nitrate, it further contains 0.5 parts by weight to 10 parts by weight of gelatin and 35 parts by weight to 70 parts by weight of nitric acid.

[0018]

The present invention further provides the method for producing highly crystalline silver powder characterized in that the first aqueous solution contains 100 parts by weight of silver nitrate, ascorbic acid contained in the second aqueous solution to be mixed with the first aqueous solution is 30 parts by weight to 90 parts by weight.

[0019]

The present invention still further provides the method for producing highly crystalline silver powder characterized in that the second aqueous solution contains 100 parts by weight of ascorbic acid, nitric acid contained in the first aqueous solution to be mixed with the second aqueous solution is 40 parts by weight to 150 parts by weight.

[0020]

The present invention also provides highly crystalline silver powder characterized in that the powder is produced by the method for producing highly crystalline silver powder.

[0021]

The highly crystalline silver powder produced by the method for producing highly crystalline silver powder is

characterized in that the powder has a crystallite

diameter of the powder is 300 Å or more.

[0022]

The highly crystalline silver powder is

characterized in that an average particle diameter D_{50} of

the powder is in the range from 0.5 μm to 10 μm. (where

D_{50} is a median diameter (μm) calculated as 50% of volume

cumulative distributions examined by a laser diffraction

scattering particle size distribution measuring method).

[0023]

The highly crystalline silver powder is

characterized in that a thermal shrinkage rate of the

powder after heating at 700°C is in the range from -3% to

3%.

[0024]

The highly crystalline silver powder is

characterized in that a ratio D_{90}/D_{10} of the powder is in

the range from 2.1 to 5.0 (where D_{10} is diameter (μm) at

10% of volume cumulative distributions and D_{90} is

diameter (μm) at 90% of volume cumulative distributions

examined by a laser diffraction scattering particle size

distribution measuring method, respectively).

[0025]

The highly crystalline silver powder is

characterized in that a crystallite diameter is 300 Å or

more, an average particle diameter D_{50} is in the range

from 0.5 μm to 10 μm, and a thermal shrinkage ratio after

heating at 700°C in the length direction is in the range from -3% to 3%.

[0026]

The highly crystalline silver powder is characterized in that a ratio D_{90}/D_{10} of the powder is in the range from 2.1 to 5.0 (where D_{10} is diameter (μm) at 10% of volume cumulative distributions and D_{90} is diameter (μm) at 90% by volume of cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

Advantage of the Invention

[0027]

Since the highly crystalline silver powder according to the present invention is of fine particles, has high dispersibility, and whose particle size distribution is not excessively sharp and relatively broad, and crystallites are large. And when it is used as a material for a conductive paste, the dispersibility of the silver powder to the conductive paste and the filling property of the conductive paste with the silver powder in can be excellent; an electrode, circuit and the like can be finer; the thick silver film obtained from the conductive paste can be excellent in thermal shrinkage resistance; and the resistivity thereof can be lowered. The method for producing the highly crystalline silver powder

according to the present invention can efficiently produce the above-described highly crystalline silver powder according to the present invention.

Best Mode for Carrying Out the Invention

[0028]

(Highly Crystalline Silver Powder According to the Present Invention)

The highly crystalline silver powder according to the present invention is substantially granular powder. The average particle diameter D_{50} of the highly crystalline silver powder according to the present invention is 0.5 μm to 10 μm, preferably 1 μm to 5 μm. It is preferable that the average particle diameter D_{50} is within the above-described range because when the silver powder is used in a conductive paste, the filling of the silver powder in the conductive paste is excellent, and the circuit or the like formed from the thick silver film can be made finer. On the other hand, the average particle diameter D_{50} less than 0.5 μm is not preferable because the collection of the silver powder becomes difficult; and the average particle diameter D_{50} exceeding 10 μm is not preferable because the silver powder is often aggregated. Here, the average particle diameter D_{50} means the volume average particle diameter measured by a laser diffraction scattering method, that is, the particle diameter at 50% cumulative distribution.

[0029]

The highly crystalline silver powder according to the present invention has a crystallite diameter of 300 Å or more, preferably 350 Å to 600 Å. It is preferable that the crystallite diameter is within the above-described range because when the conductive paste containing the silver powder is applied onto a ceramic substrate, and baked to form a circuit or the like composed of a thick silver film, the thermal shrinkage of the thick silver film between before and after baking becomes close to the thermal shrinkage of the ceramic substrate, and the effect to suppress the separation of the thick silver film from the ceramic substrate, or the deformation of the ceramic substrate due to the dimension change of the thick silver film is large.

[0030]

On the other hand, it is not preferable that the crystallite diameter is less than 300 Å, because when the conductive paste is applied onto a ceramic substrate, and baked to form a circuit or the like composed of a thick silver film, the shrinkage of the thick silver film between before and after baking becomes larger than the shrinkage of the ceramic substrate, and the thick silver film is easily separated from the ceramic substrate or the ceramic substrate is easily deformed due to the dimension change of the thick silver film. Here, the crystallite diameter means the average crystallite

diameter obtained from the half-value width of the
diffraction angle of each crystal face obtained by
conducting X-ray diffraction for silver powder sample.
[0031]

The D_{90}/D_{10} of the highly crystalline silver powder
according to the present invention is normally 2.1 to 5.0,
preferably 2.5 to 4.7. In the present invention, D_{10} is
diameter (μm) at 10% by volume cumulative distributions,
and D_{90} is diameter (μm) at 90% by volume cumulative
distributions examined by a laser diffraction scattering
particle size distribution measuring method, respectively.
The D_{90}/D_{10} is an indicator to indicate fluctuation, and a
large D_{90}/D_{10} indicates that the fluctuation of particle
size distribution is large. It is preferable that D_{90}/D_{10}
is within the above-described range, because the particle
size distribution of the silver powder is not excessively
sharp, but is relatively broad, and when a circuit is
formed with a conductive paste using the silver powder,
the filling properties of the silver powder and the
thermal shrinkage resistance of the circuit becomes
excellent, specifically the dimension change of the
circuit between before and after baking is easily reduced.
[0032]

On the other hand, it is not preferable that D_{90}/D_{10}
is less than 2.1, because the particle size distribution
becomes excessively sharp, and when a circuit is formed
with a conductive paste using the silver powder, the

filling properties of the silver powder easily becomes inferior, specifically, the dimension change of the circuit between before and after baking easily becomes large. It is also not preferable that D_{90}/D_{10} exceeds 5.0, because the particle size distribution of the silver powder becomes excessively broad to make silver powder filling properties inferior when forming a circuit using a conductive paste using the silver powder, and thus the thermal shrinkage resistance of the circuit is easily deteriorated, specifically, the dimension change of the circuit between before and after baking easily becomes large.

[0033]

The thermal shrinkage of the highly crystalline silver powder according to the present invention at 700°C in the length direction is normally in the range from -3% to 3%, preferably in the range from -2% to 2%. In the present invention, the thermal shrinkage at 700°C in the length direction means the thermal shrinkage of a pellet in the length direction measured using thermomechanical analysis (TMA) in a sample in which silver powder is formed into a pellet.

[0034]

In the highly crystalline silver powder according to the present invention, the resistivity of the silver coating film baked at a relatively low temperature, for example 300°C, is low. Specifically, even if the highly

crystalline silver powder is sintered at a low temperature, the resistivity of the sintered article can be easily reduced. The reason why the resistivity of the silver coating film thus baked at 300°C is estimated to be because the movement of electrons in the silver powder is smoothened due to large crystallite diameter.

[0035]

The specific surface area of the highly crystalline silver powder according to the present invention is normally 0.10 m^2/g to 1.0 m^2/g, preferably 0.20 m^2/g to 0.90 m^2/g. The specific surface area of less than 0.10 m^2/g is not preferable because the formation of the finer electrode or circuit composed of a thick silver film tends to be difficult. The specific surface area exceeding 1.0 m^2/g is also not preferable because the formation of paste of silver powder tends to be difficult. The specific surface area in the present invention is the BET specific surface area.

[0036]

The tap density of the highly crystalline silver powder according to the present invention is normally 3.8 g/cm^3 or more, preferably 4.0 cm^3 to 6.0 cm^3. The tap density within the above-described range is preferable because the filling of the silver powder in the paste of the highly crystalline silver powder is favorable in the preparation of the conductive paste to facilitate the preparation of the conductive paste, and on the coating

film formation of the conductive paste, adequate gaps are formed between the particles of the highly crystalline silver powder to facilitate binder removal from the coating film on baking the coating film and to improve the density of the baked film, and as a result, the resistance of the thick silver film can be easily lowered. The highly crystalline silver powder according to the present invention can be produced by the following method.

[0037]

(Method for producing the Highly Crystalline Silver Powder According to the Present Invention)

The method for producing the highly crystalline silver powder according to the present invention is to mix a first aqueous solution containing silver nitrate, a dispersing agent and nitric acid, and a second aqueous solution containing ascorbic acid.

[0038]

The first aqueous solution in the present invention is an aqueous solution containing silver nitrate, a dispersing agent and nitric acid. As the water used for the preparation of the first aqueous solution, pure water, ion-exchanged water, ultra-pure water or the like is preferable for preventing impurities to be mixed. The silver nitrate used in the present invention is not specifically limited, but either solid or an aqueous solution can be used.

[0039]

The examples of dispersing agents used in the present invention include polyvinylpyrrolidone (PVP), gelatin, polyethylene glycol, polyvinyl alcohol and the like. In the present invention, the term "gelatin" is used in the concept including glue. Among the dispersing agents used in the present invention, polyvinylpyrrolidone and gelatin are preferable because the thermal shrinkage resistance of silver powder can be particularly elevated. In the present invention, by compounding the dispersing agent in the first aqueous solution, the dispersion of the silver powder can be improved, and there is the effect of making the silver powder have fine particles, and making the particle size distribution not excessively sharp and relatively broad.

[0040]

The nitric acid used in the present invention is not specifically limited, but either concentrated nitric acid or diluted nitric acid can be used. In the present invention, since the rate of the reaction to form silver from silver ions is controlled to be relatively slow by compounding sulfuric acid in the first aqueous solution, there is the effect of making the particle size distribution not excessively sharp and relatively broad, and enlarging the crystallites. If silver powder is produced without compounding nitric acid, the rate of the reaction to form silver from silver ions is excessively rapid and the reaction starts immediately, the obtained

silver powder has a smaller particle diameters, and the crystallite diameter tends to be reduced compared with the case to produce the silver powder by compounding nitric acid as in the present invention.

[0041]

When the dispersing agent is polyvinylpyrrolidone, the first aqueous solution contains normally 5 parts by weight to 60 parts by weight, preferably 15 parts by weight to 50 parts by weight, and more preferably 20 parts by weight to 40 parts by weight of polyvinylpyrrolidone to 100 parts by weight of silver nitrate. It is preferable that the compounding quantity of polyvinylpyrrolidone is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of polyvinylpyrrolidone is less than 5 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of polyvinylpyrrolidone exceeds 60 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

[0042]

When the dispersing agent is gelatin, the first aqueous solution contains normally 0.5 part by weight to 10 parts by weight, preferably 1 part by weight to 8 parts by weight, and more preferably 2 parts by weight to 6 parts by weight of gelatin to 100 parts by weight of silver nitrate. It is preferable that the compounding quantity of gelatin is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of gelatin is less than 0.5 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of gelatin exceeds 10 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

[0043]

When the dispersing agent is polyvinylpyrrolidone, the first aqueous solution contains normally 1 part by weight to 10 parts by weight, preferably 2 parts by weight to 4 parts by weight of gelatin to 100 parts by weight of water. It is preferable that the compounding quantity of polyvinylpyrrolidone is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of

the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of polyvinylpyrrolidone is less than 1 parts by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of polyvinylpyrrolidone exceeds 10 parts by weight, because the impurity concentration in the obtained silver powder is easily elevated, environment is easily contaminated, and the production costs tend to be high.

[0044]

When the dispersing agent is gelatin, the first aqueous solution contains normally 0.1 parts by weight to 5 parts by weight, preferably 0.4 parts by weight to 2 parts by weight of gelatin to 100 parts by weight of water. It is preferable that the compounding quantity of gelatin is within the above-described range, because the dispersion of the silver powder is improved, and the particle size distribution of the silver powder tends to be not excessively sharp but to be relatively broad. On the other hand, it is not preferable that the compounding quantity of gelatin is less than 0.1 part by weight, because the obtained silver powder is easily aggregated; and it is not preferable that the compounding quantity of gelatin exceeds 5 parts by weight, because the impurity concentration in the obtained silver powder is easily

elevated, environment is easily contaminated, and the
production costs tend to be high.

[0045]

The first aqueous solution contains normally 35
parts by weight to 70 parts by weight, preferably 40
parts by weight to 60 parts by weight, and more
preferably 48 parts by weight to 54 parts by weight of
nitric acid to 100 parts by weight of silver nitrate. It
is preferable that the compounding quantity of nitric
acid is within the above-described range, because the
dispersion of the silver powder is improved, and the
particle size distribution of the silver powder tends to
be not excessively sharp but to be relatively broad. On
the other hand, it is not preferable that the compounding
quantity of nitric acid is less than 35 parts by weight,
because the crystallization ability of the silver powder
is easily lowered; and it is not preferable that the
compounding quantity of nitric acid exceeds 70 parts by
weight, because the obtained silver powder is easily
aggregated. In the present invention, the compounding
quantity of nitric acid means the compounding quantity
converted to concentrate nitric acid of a concentration
of 61%.

[0046]

The second aqueous solution in the present invention
is an aqueous solution containing ascorbic acid. As the
water used for the preparation of the first aqueous

solution, pure water, ion-exchanged water, ultra-pure water or the like is preferable for preventing impurities to be mixed. As the ascorbic acid used in the present invention, either L-isomer or D-isomer can be used.

[0047]

In the production method according to the present invention, the above-described first aqueous solution and second aqueous solution are mixed to deposit highly crystalline silver powder in the blended solution. The examples of mixing modes include a method wherein the first aqueous solution is agitated and the second aqueous solution is mixed thereto. As the method to add the second aqueous solution, the entire quantity of the second aqueous solution can be added to the first aqueous solution at once, or the second aqueous solution can be gradually added to the first aqueous solution a little at a time. When the dispersing agent in the first aqueous solution is polyvinylpyrrolidone, the method to add the entire quantity of the second aqueous solution to the first aqueous solution is preferable because the silver powder composed of fine particles, whose particle size distribution is not excessively sharp but is relatively broad can be easily obtained; when the dispersing agent in the first aqueous solution is gelatin, the method to add the second aqueous solution gradually to the first aqueous solution a little at a time is preferable because

the particle diameter of silver powder can be easily
controlled.

[0048]

In mixing the first aqueous solution and the second
aqueous solution, the solutions are mixed so that the
quantity of ascorbic acid contained in the second aqueous
solution is normally 30 parts by weight to 90 parts by
weight, preferably 40 parts by weight to 80 parts by
weight, and more preferably 50 parts by weight to 75
parts by weight to 100 parts by weight of silver nitrate
contained in the first aqueous solution. It is
preferable that the compounding quantity of ascorbic acid
to silver nitrate is within the above-described range
because the yield of the silver powder is easily elevated.
On the other hand, it is not preferable that the
compounding quantity of ascorbic acid to 100 parts by
weight silver nitrate is less than 30 parts by weight,
because reduction is insufficient and the yield of the
silver powder is easily lowered; and it is not preferable
that the compounding quantity of ascorbic acid to 100
parts by weight silver nitrate exceeds 90 parts by weight,
because environment is easily contaminated, and the
production costs tend to be high.

[0049]

In mixing the first aqueous solution and the second
aqueous solution, the solutions are mixed so that the
silver ion concentration in the obtained mixed solution

is normally 10 g/l to 80 g/l, preferably 30 g/l to 65 g/l.
It is preferable that the silver ion concentration in the
blended solution is within the above-described range
because the yield of the silver powder is high and the
obtained silver powder is difficult to aggregate. On the
other hand, it is not preferable that the silver ion
concentration is less than 10 g/l, the productivity of
the silver powder tends to be worsened; and it is not
preferable that the silver ion concentration exceeds 80
g/l, the silver powder is easily aggregated.

[0050]

In mixing the first aqueous solution and the second
aqueous solution, the solutions are mixed so that the
quantity of nitric acid contained in the first aqueous
solution is normally 40 parts by weight to 150 parts by
weight, preferably 50 parts by weight to 120 parts by
weight, and more preferably 65 parts by weight to 100
parts by weight to 100 parts by weight of ascorbic acid
contained in the second aqueous solution. It is
preferable that the compounding quantity of nitric acid
to ascorbic acid is within the above-described range
because the yield of the silver powder is easily elevated.
On the other hand, it is not preferable that the
compounding quantity of nitric acid to 100 parts by
weight ascorbic acid is less than 40 parts by weight,
because it is difficult to sufficiently increase the
crystallite diameter of the obtained silver powder; and

it is not preferable that the compounding quantity of
nitric acid to 100 parts by weight ascorbic acid exceeds
150 parts by weight, the obtained silver powder is easily
aggregated.

[0051]

It is preferable that silver powder deposited in the
blended solution by mixing the first aqueous. solution and
the second aqueous solution is grown in the blended
solution by continuing agitation normally for further 3
minutes or more, preferably 5 minutes to 10 minutes,
because the particle diameter, particle size distribution
and dispersion of the silver powder are easily within the
specific ranges of the silver powder according to the
present invention. After filtering the silver powder
obtained in the blended solution using filtering means,
for example, a Nutsche, the filtered product is washed
with pure water and dried to obtain the highly
crystalline silver powder according to the present
invention.

[0052]

The above-described highly crystalline silver powder
according to the present invention can be used as the
material for a conductive paste that can form electrodes
or circuits of, for example, chip devices, plasma display
panels, glass ceramic packages, ceramic filters and the
like; in particular, it can be suitably used as the
material for a conductive paste not only for ordinary

ceramic substrates, but also for LTCC substrates as
substrates forming the circuit, utilizing the very small
thermal shrinkage of the silver powder. The method for
producing highly crystalline silver powder according to
the present invention can also be used for producing
highly crystalline silver powder according to the present
invention.

[0053]

Although the examples will be described below, these
examples should not be construed to limit the present
invention.

Example 1

[0054]

10 g of PVP (K-value: 30), 50g of silver nitrate and
24.6 g of concentrated nitric acid (concentration: 61wt%)
were added into 500 g of pure water at room temperature,
and dissolved by stirring to prepare a first aqueous
solution (first aqueous solution A). In addition, 35.8 g
of ascorbic acid was added into 500 g of pure water at
room temperature, and dissolved by stirring to prepare a
second aqueous solution (second aqueous solution A). The
compositions of the first aqueous solution and the second
aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution A was added to the
stirring first aqueous solution A at once, after that,
stirring was continued for 5 minutes to grow particles in
the blended solution. Thereafter, stirring was stopped

to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, D_{10}, D_{50}, D_{90}, D_{100}, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured using the following methods and D_{90}/D_{10} was calculated. The results are shown in Table 3 to Table 6.

[0055]

(D_{10}, D_{50}, D_{90}, D_{100}, SD): 10%, 50%, 90% and 100% were indicated as D_{10} (μm), D_{50} (μm), D_{90} (μm), D_{100} (μm) are particle diameters when the cumulative distributions measured by a laser diffraction scattering method using [Micro Track HRA] manufactured by Nikkiso Co., Ltd. were, respectively, and SD is the standard deviation in the particle size distribution.

(Crystallite diameter): X-ray diffraction on the powder was performed using an X-ray diffraction apparatus [RINT 2000/PC] manufactured by Rigaku Corporation, and the crystallite diameter was calculated from the half-value width of the peak of diffraction angle obtained on each crystal faces.

(Specific surface area): It is a B.E.T. specific surface area measured by [Monosorb] manufactured by Yuasa-Ionics Co., Ltd.

(Tap density): Tap density was measured by tapping the sample using [Tap Denser] manufactured by Kuramochi Kagaku Kikai Seisakusyo Co., Ltd.

(Thermal shrinkage): A columnar pellet was prepared by compressing the silver powder, and the TMA analysis of the pellet was conducted using TMA/SS 6300 manufactured by Seiko Instruments Inc., in air at a temperature elevation rate of 10°C/min within the range between room temperature and 850°C to measure thermal shrinkage of the pellet in the length direction. The measuring temperatures were 300°C, 500°C and 700°C.

(Resistivity): A mixed solvent was prepared by mixing 95 parts by weight of terpineol and 5 parts by weight of ethyl cellulose, a paste was prepared by mixing 15 parts by weight of the mixed solvent and 85 parts by weight of the sample powder, and the paste was baked at 300°C to prepare a silver coating film having a thickness of about several μm. Other silver coating films were prepared in the same manner as described above except that the baking temperatures were 400°C and 500°C instead of 300°C.

Then, after measuring the resistance (Ω) of the silver coating films by four-terminal network method using (MILLIOHM METER manufactured by Hewlett-Packard), the resistivity ρ ($\Omega \cdot m$) was obtained from the cross-

sectional area of the silver coating films and the length between the terminals.

Example 2

[0056]

20 g of PVP (K-value: 30), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a first aqueous solution (first aqueous solution B). In addition, 35.8 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution A). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution A was added to the first aqueous solution B in at once, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was filtered using a Nutsche. Then, the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, D_{10}, D_{50}, D_{90}, D_{100}, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods

and D_{90}/D_{10} was calculated. The results are shown in Table 3 to Table 6.

Comparative Example 1

[0057]

10 g of PVP (K-value: 30) and 50g of silver nitrate were added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a first aqueous solution (first aqueous solution C). In addition, 26 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution B). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution B was added to the stirring first aqueous solution C at once, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, D_{10}, D_{50}, D_{90}, D_{100}, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods

and D_{90}/D_{10} was calculated. The results are shown in Table 3 to Table 6.

Example 3

[0058]

1.0 g of gelatin (manufactured by Nitta Gelatin Inc.), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 250 g of pure water at room temperature, and then, heated up to 50°C and dissolved by stirring to prepare a first aqueous solution (first aqueous solution D). In addition, 26.4 g of ascorbic acid was added into 250 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution C). The compositions of the first aqueous solution D and the second aqueous solution C are shown in Table 1 and Table 2.

Next, the second aqueous solution C at room temperature was gradually added to the stirring first aqueous solution D at 50°C in 30 minutes, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution was filtered using a Nutsche. Then the filtered product was rinsed with pure water and dried, and then highly crystalline silver powder was obtained.

For the obtained silver powder, D_{10}, D_{50}, D_{90}, D_{100}, SD, crystallite diameter, specific surface area, tap density, thermal shrinkage and resistivity were measured in the same manner as in Example 1 using the following methods and D_{90}/D_{10} was calculated. The results are shown in Table 3 to Table 6.

Example 4

[0059]

3.0 g of gelatin (manufactured by Nitta Gelatin Inc.), 50g of silver nitrate and 24.6 g of concentrated nitric acid (concentration: 61%) were added into 500 g of pure water at room temperature, and then, heated up to 50°C and dissolved by stirring to prepare a first aqueous solution (first aqueous solution E). In addition, 25.9 g of ascorbic acid was added into 500 g of pure water at room temperature, and dissolved by stirring to prepare a second aqueous solution (second aqueous solution D). The compositions of the first aqueous solution and the second aqueous solution are shown in Table 1 and Table 2.

Next, the second aqueous solution D at room temperature was gradually added to the stirring first aqueous solution E in 30 minutes, after that, stirring was continued for 5 minutes to grow particles in the blended solution. Thereafter, stirring was stopped to settle the particles in the blended solution. After settling the particles, the supernatant of the blended solution was disposed, and the rest of blended solution

was filtered using a Nutsche. Then the filtered product
was rinsed with pure water and dried, and then highly
crystalline silver powder was obtained.

For the obtained silver powder, D_{10}, D_{50}, D_{90}, D_{100}, SD,
crystallite diameter, specific surface area, tap density,
thermal shrinkage and resistivity were measured in the
same manner as in Example 1 using the following methods
and D_{90}/D_{10} was calculated. The results are shown in
Table 3 to Table 6.

[0060]

[Table 1]

	Water (g)	Kind of dispersing agent	Dispersing agent (g)	Silver nitrate (g)	Concentrated nitric acid (g)	Kind of first aqueous solutions
Example 1	500	PVP	10	50	24.6	A
Example 2	500	PVP	20	50	24.6	B
Comparative Example 1	500	PVP	10	50	0	C
Example 3	250	Gelatin	1.0	50	26.4	D
Example 4	500	Gelatin	3.0	50	24.6	E

[0061]

[Table 2]

	Water (g)	Ascorbic acid (g)	Kind of second aqueous solutions
Example 1	500	35.8	A
Example 2	500	35.8	A
Comparative Example 1	500	26.0	B
Example 3	250	26.4	C
Example 4	500	25.9	D

[0062]

[Table 3]

	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	D_{100} (μm)	D_{90}/D_{10}	SD
Example 1	2.97	6.35	10.75	22.0	3.6	3.01
Example 2	1.30	3.03	5.67	15.6	4.4	1.59
Comparative Example 1	2.14	2.83	4.08	9.3	1.9	0.71
Example 3	2.72	4.36	7.33	18.5	2.7	1.71
Example 4	0.76	1.27	2.28	4.6	3.0	0.57

[0063]

[Table 4]

	Crystallite diameter (Å)	Specific surface area (m^2/g)	Tap density (g/cm^3)
Example 1	441	0.30	4.1
Example 2	377	0.62	4.0
Comparative Example 1	258	0.62	3.8
Example 3	545	0.20	4.4
Example 4	441	0.72	4.8

[0064]

[Table 5]

	Thermal shrinkage percentage at 300°C (%)	Thermal shrinkage percentage at 500°C (%)	Thermal shrinkage percentage at 700°C (%)
Example 1	0.13	-2.13	-2.2
Example 2	0.09	-2.68	-2.9
Comparative Example 1	0.84	-4.02	-7.82
Example 3	0.27	1.08	1.13
Example 4	-0.58	-1.51	-1.35

[0065]

[Table 6]

	Resistivity of silver coating film baked at 300°C ρ(Ω·m)	Resistivity of silver coating film baked at 400°C ρ(Ω·m)	Resistivity of silver coating film baked at 500°C ρ(Ω·m)
Example 1	$4.1×10^{-5}$	$2.0×10^{-5}$	$9.9×10^{-6}$
Example 2	$5.2×10^{-5}$	$1.5×10^{-5}$	$1.2×10^{-5}$
Comparative Example 1	$7.2×10^{-4}$	$8.9×10^{-6}$	$4.8×10^{-5}$
Example 3	$9.4×10^{-6}$	$8.3×10^{-6}$	$9.9×10^{-6}$
Example 4	$1.0×10^{-5}$	$8.8×10^{-6}$	$4.8×10^{-5}$

[0066]

From Table 1 to Table 5, it is clearly shown that silver powder prepared by using both dispersing agent and nitric acid is highly crystalline with a large crystallite diameter, and thermal shrinkage after heating at 700°C is small. Especially when gelatin is used as the dispersing agent, thermal shrinkage after heating at 700°C is especially small. From Table 6, it is found that silver powder prepared by using both dispersing agent and nitric acid show lower resistivity ρ on the silver coating film after baked at 300°C when compared with the silver powder prepared without using nitric acid. The reason why is suspected that the movement of electrons in the silver powder of the invention is more smooth because of it is large crystallite diameter.

Industrial Applicability

[0067]

The highly crystalline silver powder according to the present invention is useful for the material to be contained in a conductive paste for forming electrodes and/or circuits, for example, chip devices, plasma display panels, glass ceramic packages, ceramic filters and the like. Also the method for producing highly crystalline silver powder according to the present

invention is useful. Especially, it is shows good performance on LTCC substrate.

CLAIMS

1.   A method for producing highly crystalline silver powder which is characterized in that mixing a first aqueous solution and a second aqueous solution, wherein the first aqueous solution contains silver nitrate, a dispersing agent and nitric acid, and the second solution contains ascorbic acid.

2.   The method for producing highly crystalline silver powder according to claim 1, wherein the dispersing agent is polyvinylpyrrolidone.

3.   The method for producing highly crystalline silver powder according to claim 1, wherein the dispersing agent is a gelatin.

4.   The method for producing highly crystalline silver powder according to claim 2, the first aqueous solution when it contains 100 parts by weight of silver nitrate, it further contains 5 parts by weight to 60 parts by weight of polyvinylpyrrolidone and 35 parts by weight to 70 parts by weight of nitric acid.

5.   The method for producing highly crystalline silver powder according to claim 3, the first aqueous solution when it contains 100 parts by weight of silver nitrate,

it further contains 0.5 parts by weight to 10 parts by weight of gelatin and 35 parts by weight to 70 parts by weight of nitric acid.

6.   The method for producing highly crystalline silver powder according to claim 1, when the first aqueous solution contains 100 parts by weight of silver nitrate, ascorbic acid contained in the second aqueous solution to be mixed with the first aqueous solution is 30 parts by weight to 90 parts by weight.

7.   The method for producing highly crystalline silver powder according to claim 1, when the second aqueous solution contains 100 parts by weight of ascorbic acid, nitric acid contained in the first aqueous solution to be mixed with the second aqueous solution is 40 parts by weight to 150 parts by weight.

8.   Highly crystalline silver powder which is characterized in that the powder is produced by the method according to claim 1.

9.   The highly crystalline silver powder according to claim 8, wherein crystallite diameter of the powder is 300 Å or more.

10. The highly crystalline silver powder according to claim 8, wherein an average particle diameter D_{50} of the powder is in the range from 0.5 μm to 10 μm. (where D_{50} is a median diameter (μm) calculated as 50% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method).

11. The highly crystalline silver powder according to claim 8, wherein a thermal shrinkage rate of the powder after heating at 700°C is in the range from -3% to 3%.

12. The highly crystalline silver powder according to claim 8, wherein a ratio D_{90}/D_{10} of the powder is in the range from 2.1 to 5.0 (where D_{10} is diameter (μm) at 10% of volume cumulative distributions and D_{90} is diameter (μm) at 90% of volume cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

13. Highly crystalline silver powder which is characterized in that a crystallite diameter is 300 Å or more, an average particle diameter D_{50} is in the range from 0.5 μm to 10 μm, and a thermal shrinkage ratio after heating at 700°C in the length direction is in the range from -3% to 3%.

14. The highly crystalline silver powder according to claim 13, wherein a ratio D_{90}/D_{10} of the powder is in the range from 2.1 to 5.0 (where D_{10} is diameter (μm) at 10% of volume cumulative distributions and D_{90} is diameter (μm) at 90% by volume of cumulative distributions examined by a laser diffraction scattering particle size distribution measuring method, respectively).

ABSTRACT

An object of the present invention is to provide highly crystalline silver powder which is characterized in fine particles, showing high dispersibility, it's particle size distribution is not excessively sharp but relatively broad and crystallites are large; and a method for producing the same. In order to achieve the object, a method for producing highly crystalline silver powder is characterized in that mixing a first aqueous solution and a second aqueous solution, wherein the first aqueous solution contains silver nitrate, a dispersing agent and nitric acid, and the second solution contains ascorbic acid. For dispersing agent, polyvinylpyrrolidone or gelatin is preferred. Highly crystalline silver powder produced by the above-described method is preferred to be a crystallite diameter of 300 Å or more, an average particle diameter D_{50} in the range from 0.5 μm to 10 μm, and a thermal shrinkage rate for the length direction after heating at 700°C in the range from -3% to 3%. For ratio D_{90}/D_{10} of the silver powder is preferred to be in the range from 2.1 to 5.0.